



Removal of aqueous organic pollutants by adsorption-catalytic process using mesoporous carbon beads loaded with metal oxides

Takuji Yamamoto^{*}, Seong-Ick Kim, Jintawat Chaichanawong, Eiad-ua Apiluck, Takao Ohmori

National Institute of Advanced Industrial Science and Technology (AIST), Central 5, 1-1-1 Higashi, Tsukuba, Ibaraki 305-8565, Japan

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ABSTRACT

Removal of aqueous organic pollutants using an adsorption-catalytic process was examined using metal-loaded carbon cryogel beads (CCBs) which possess numerous mesopores of controlled size. Adsorption isotherms of phenol, as a model organic pollutant, on CCBs could be interpreted based on the Langmuir model, indicating the preferable adsorption of phenol on micropores rather than on mesopores. Removal of aqueous phenol was examined using metal oxide-loaded CCBs in the presence of ozone. Due to the adsorptive-concentration effect of CCBs, it proved possible to increase the phenol removal efficiency by the simultaneous use of ozone with CCBs as compared with ozone only. Of the support materials for loading metal oxides, CCBs showed the highest removal efficiency. The enhancement effect of CCBs in the removal of aqueous phenol was examined with regard to the metal species loaded, the amount of loaded metal, the size of the mesopores, and the carbonization temperature used in the preparation of CCBs.

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1. Introduction

Control of water quality is becoming a significant problem in many areas. To ensure the protection of natural water resources as well as establishing sustainable water supply systems, it is essential to develop efficient water treatment processes. Since persistent organic substances biodegrade slowly and are highly toxic, they cause significant damage to natural water systems and consequently to human health. For the removal of such organic substances, conventional water treatment methods such as adsorption, biodegradation or chemical oxidation are, however, not efficient. To improve treatment efficiency, advanced oxidation processes (AOPs), based on the in situ generation of strong oxidants such as hydroxyl radicals, have been studied in the last decade using various combinations of ozone, hydrogen peroxide, UV, ultrasound, supercritical water, pulsed corona discharges, electron beam irradiation, etc. [1–6]. One of the most intensively studied AOPs is a process based on the Fenton reaction, which uses hydrogen peroxide as an oxidizer in the presence of catalysts [7–10]. Recently, electron-Fenton degradation was reported as a novel and efficient AOP to purify wastewater containing organic chemicals used as antimicrobials [11,12]. In some Fenton processes, porous materials such as zeolite [9,13] or porous alumina [7] are used as support materials for metal catalysts.

Use of a porous material that can be employed both as an adsorbent and a support material can increase treatment efficiency. An adsorption-catalytic process (ACP) such as this is an effective water treatment method in cases where pollutants are concentrated by adsorption on the porous material. Photocatalytic degradation of organic pollutants using TiO_2 under UV light irradiation is regarded as one form of ACP [14,15]. The simultaneous use of ozone with a porous catalyst is also a potential ACP, in which a porous adsorbent is used to concentrate dilute pollutants dissolved in water [16,17]. Activated carbon is one of the most practical adsorbents and is utilized both in industrial and commercial water treatment processes. Due to its large surface area, activated carbon is often used as an adsorbent or support material for catalysts. However, depending on the molecular size of pollutants, the sizes of pores in activated carbon are too small to be used as adsorbents in the liquid phase, since diffusion of reactants or products inside micropores tends to be quite slow, which is not advantageous for efficient treatment of wastewater. For this reason, porous carbon with a relatively large pore size is regarded as a potential adsorbent or support material for catalysts for use in ACP.

For this purpose, we regard porous carbon, which possesses a developed and controlled mesoporous structure, to be suitable. A carbon cryogel can be synthesized through the sol-gel polycondensation of, for example, resorcinol with formaldehyde in a slightly basic aqueous solution, followed by freeze-drying and pyrolysis in an inert atmosphere [18]. One of the most unique properties of carbon cryogels is the adjustability of their mesopores by varying the

^{*} Corresponding author. Tel.: +81 29 861 7896; fax: +81 29 861 4660.

E-mail address: yamamoto-t@aist.go.jp (T. Yamamoto).

Nomenclature

C	concentration of aqueous phenol, ppm
C_0	initial concentration of aqueous phenol, ppm
k	removal rate constant of aqueous phenol, min^{-1}
n	order of removal process of phenol
p/p_0	relative pressure of nitrogen gas
q	amount of adsorbed phenol, mg g^{-1}
q_{N_2}	amount of adsorbed nitrogen, $\text{cm}^3 \text{g}^{-1}$
R/C	molar ratio of resorcinol to catalyst used for preparation of CCBs
R_{leach}	leached amount of metal, %
R_{load}	loaded amount of metal, %
R_p	radius of mesopores, nm
R_{peak}	peak radius of mesopore size distribution, nm
S_{BET}	BET specific surface area, $\text{m}^2 \text{g}^{-1}$
t	treatment time, min
T_p	carbonization temperature, $^{\circ}\text{C}$
V_{mes}	mesopore volume, $\text{cm}^3 \text{g}^{-1}$
V_{mic}	micropore volume, $\text{cm}^3 \text{g}^{-1}$
V_p	pore volume, $\text{cm}^3 \text{g}^{-1}$

concentration of the base used as a catalyst during the sol-gel polycondensation process. As illustrated in Fig. 1, a carbon cryogel possesses a unique network structure that is formed by interconnected primary particles. Mesopores formed between the primary particles can act as sites for loading metal catalysts as well as diffusion paths of reactants or products. Micropores present inside each primary particle can also act as adsorption sites for pollutants. The porous structure of a carbon cryogel is potentially advantageous as an adsorbent and as a support material for catalysts for treating wastewater containing organic pollutants.

In a previous study, we researched the adsorption characteristics of a carbon cryogel with a different porous structure in the liquid phase. The amounts of adsorbed aqueous organic substances (phenol and reactive dyes) have been confirmed to be related to the size of the mesopores in the carbon cryogels [19]. In the present study, we attempted the removal of aqueous phenol using an adsorption-catalytic process employing a carbon cryogel. The effect of loading metal oxide on the carbon cryogel was initially examined from the adsorption characteristics in the liquid phase. Next, removal of aqueous phenol was examined by the simultaneous use of ozone and carbon cryogel beads (CCBs) loaded with metal oxides. To facilitate the handling of adsorbents in water as well as to remove the influence of a particle size distribution on intra-particle diffusion, CCBs with a uniform particle size were used. The performance of CCBs as a support material for metal oxides was evaluated by comparing it with that of silica gel beads and activated carbon beads. The effects of various conditions for preparation of metal-loaded CCBs on the removal efficiency of aqueous phenol were then examined.

2. Experimental

2.1. Preparation and characterization of CCBs

The synthetic procedure and the image of CCBs are shown in Fig. 2. Spherical and fairly monodisperse CCBs could be obtained based on the SI method. The details of procedures to control the size and shape of CCBs have been previously reported [20]. Resorcinol (R) and formaldehyde (F) are used as raw materials.

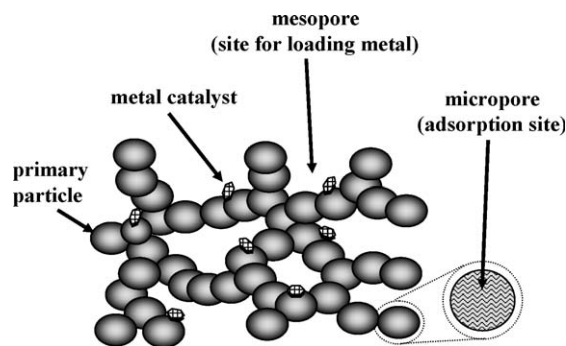


Fig. 1. Network structure formed in carbon cryogel.

Sodium carbonate (C) was used as a catalyst for the sol-gel polycondensation of resorcinol with formaldehyde. All chemicals were of research grade and were purchased from Wako Pure Chemical Industries, Ltd. The molar ratio of resorcinol to sodium

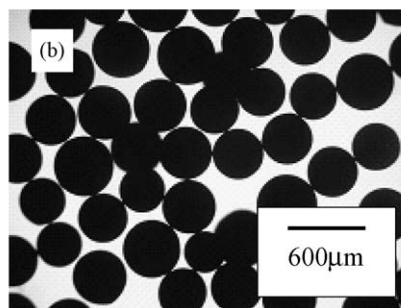
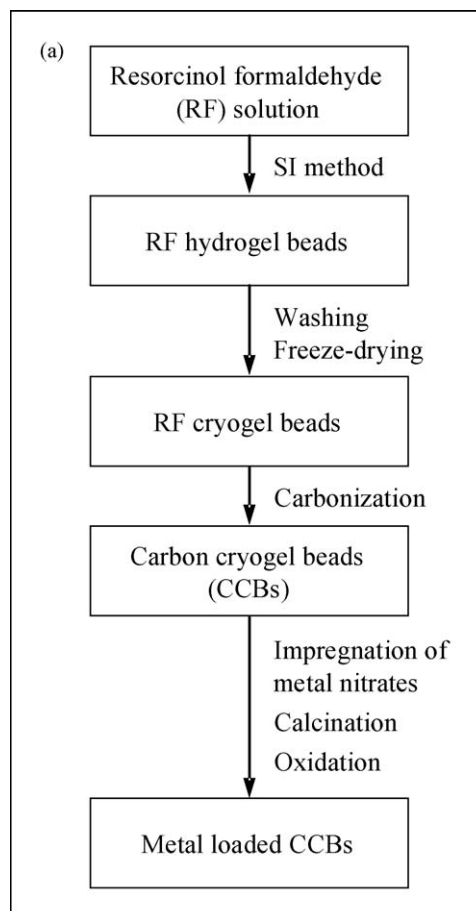


Fig. 2. (a) Synthetic procedure of CCBs and (b) optical microscope image of CCBs.

carbonate (R/C) was varied between 200 and 800 to dictate the porous structure of the CCBs. The carbonization temperature for preparation of CCBs was varied from 600 to 1400 °C. The prepared CCBs were labeled as, for instance, CCBs_{400–1000}, indicating that the R/C ratio is 400 and carbonization temperature is 1000 °C.

Metal oxides were loaded on the CCBs by impregnation. First, the CCBs were immersed in aqueous solutions of Ni(NO₃)₂, Co(NO₃)₂, Fe(NO₃)₃ or Mn(NO₃)₂. The concentration of each metal nitrate was adjusted so as to load the required amount of metal oxide at a selected rate of 0.5–5 wt.% of the weight of raw CCBs. The mixture was then dried in a rotary evaporator. Next, it was calcined at 500 °C in flowing nitrogen gas for 5 h to decompose the metal nitrates. Finally, the metal-loaded CCBs were heated at 200 °C in flowing air for 2 h to oxidize the loaded metal. The catalysts prepared in this way were labeled as, for example, 1%Ni/CCBs, indicating CCBs containing 1 wt.% of nickel oxide. Silica gel beads (Q15, supplied from Fuji Silysia Chemical Ltd.) possessing almost the same pore diameter and mesopore volume as CCBs_{400–1000}, and activated carbon beads (G-70R, supplied from Kureha Corp.) with developed micropores were also used as support materials.

The porous properties of the materials were determined by volumetric gas adsorption measurement at –196 °C using an automatic gas adsorption–desorption apparatus (Belsorp-28SA, Bel Japan, Inc.).

2.2. Liquid phase adsorption of phenol using CCBs

Twenty-milligram samples of CCBs were placed in a glass vial containing 40 cm³ of an aqueous solution of phenol at different initial concentrations of 12.5–400 ppm. After shaking the vial at 30 °C for 4 days, the equilibrium concentration of the residual phenol in the aqueous phase was measured using a UV absorption spectrophotometer (UV-2550/2450, Shimadzu Corporation).

2.3. Degradation of aqueous phenol by simultaneous use of ozone with CCBs

Fig. 3 shows a batch reactor used for removal of aqueous phenol by simultaneous use of ozone with CCBs. The experimental

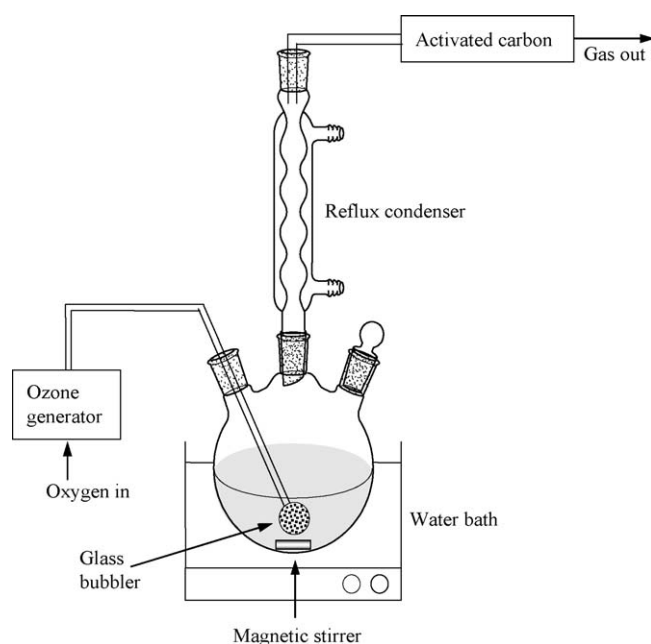


Fig. 3. Experimental setup used for removal of aqueous phenol.

Table 1

Experimental condition for degradation of aqueous phenol.

Parameter	Condition
Initial concentration of phenol	100 (ppm)
Reaction temperature	30 (°C)
Flow rate of O ₃ /O ₂ into a reactor	500 (cm ³ min ^{−1})
Weight of added CCBs	0.5 (g)

conditions are summarized in Table 1. Oxygen gas containing ozone was bubbled through the solution via a porous glass sponge installed at the bottom of the reactor, which was immersed in a thermally controlled water bath. The average ozone concentration supplied to the reactor was around 2 ppm. During the treatment, the CCBs were agitated using a magnetic stirrer set at 200 rpm. The change of phenol concentration with elapse of time was then measured using a high performance liquid chromatograph (HPLC) (LC-10A, Shimadzu Corp.) and a TOC analyzer (Sievers 900, GE Analytical Instruments).

The stability of the metal oxides loaded on the CCBs was evaluated by a leaching test. The amount of metal leached from CCBs to the treated solution during ozonation was measured using a radiofrequency inductively coupled plasma (ICP) atomic emission spectrometer (Ultima2, Horiba, Ltd.).

3. Results and discussion

3.1. Porous properties and adsorption characteristics of CCBs

The porous properties of the support materials and catalysts used in this study are summarized in Table 2. Since the network structure of CCBs is almost entirely determined during the sol–gel polycondensation, the mesopores formed in the network structure are highly dependent on the molar ratio of resorcinol to catalyst (R/C). As shown in Table 2, sizes of mesopores (R_{peak}) in the CCBs increases with increased R/C ratio. It is clear that the volume of micropores (V_{mic}) decreases with increasing carbonization temperature (T_p).

Fig. 4 shows examples of adsorption and desorption isotherms of nitrogen on CCBs_{400–1000} and 1%Ni/CCBs_{400–1000}. The pore size distributions obtained by analysis of the isotherms are also depicted. In a relatively low pressure range ($p/p_0 \approx 0$), the isotherms on 1%Ni/CCBs_{400–1000} nearly coincide with those on CCBs_{400–1000}, indicating that micropores of CCBs_{400–1000} are little affected by loading with metal oxides. On the other hand, in the relatively high pressure range of $p/p_0 \approx 1$, the amount of nitrogen adsorbed on 1%Ni/CCBs_{400–1000} is lower than that on CCBs_{400–1000}. These results confirm that metal oxides are loaded on the mesopores of CCBs as depicted in Fig. 1.

Fig. 5 shows adsorption isotherms of aqueous phenol on CCBs_{400–1000}, 1%Ni/CCBs_{400–1000} and 1%Fe/CCBs_{400–1000}. These isotherms can be interpreted using the Langmuir model, which indicates favorable adsorption on microporous materials. Since the amount of phenol adsorbed is virtually unchanged by loading metal oxides, phenol molecules are considered to adsorb preferably on the micropores.

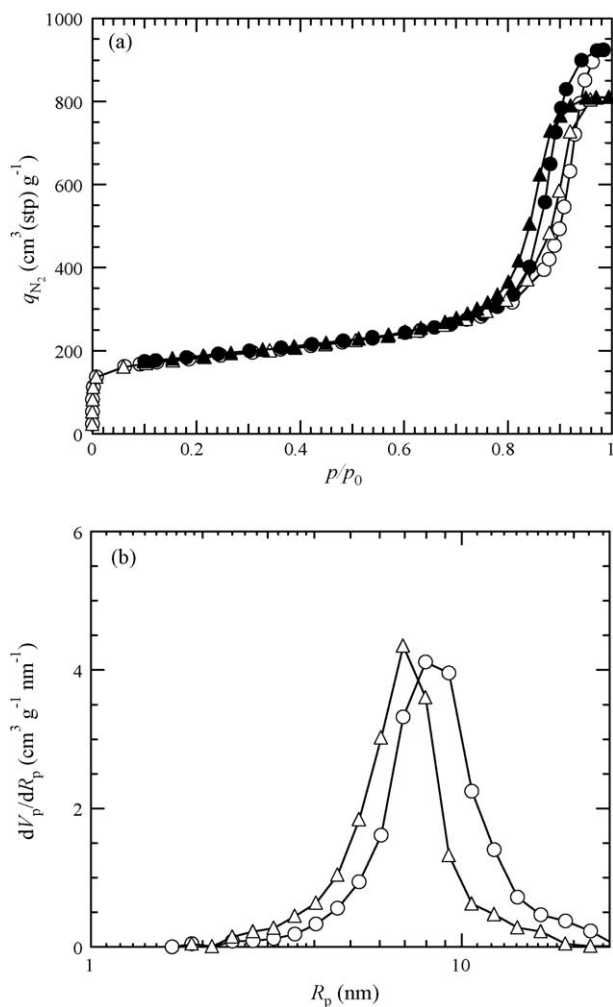
3.2. Removal of aqueous phenol by simultaneous use of CCBs and ozone

Initially, the adsorptive-concentration effect of CCBs on the removal efficiency of aqueous phenol was examined using 1%Ni/CCBs_{400–1000} as an example. Fig. 6(a) shows the decay of phenol concentration during ozonation. In Fig. 6(b), the horizontal and vertical axes correspond respectively to the concentration of

Table 2

Synthetic conditions and physical properties of porous materials.

Sample	R/C	T_p (°C)	R_{load}^a (%)	S_{BET}^b (m ² g ⁻¹)	R_{peak}^c (nm)	V_{mes}^d (cm ³ g ⁻¹)	V_{mic}^e (cm ³ g ⁻¹)
CCBs ₂₀₀₋₁₀₀₀	200	1000	–	710	6.9	1.32	0.13
CCBs ₄₀₀₋₁₀₀₀	400	1000	–	642	8.0	1.28	0.15
CCBs ₈₀₀₋₁₀₀₀	800	1000	–	616	25.8	2.43	0.19
CCBs ₄₀₀₋₆₀₀	400	600	–	767	10.6	1.55	0.20
CCBs ₄₀₀₋₁₄₀₀	400	1400	–	454	8.0	1.28	0.07
1%Ni/CCBs ₄₀₀₋₁₀₀₀	400	1000	1.0	640	7.0	1.11	0.15
1%Co/CCBs ₄₀₀₋₁₀₀₀	400	1000	1.0	652	6.9	1.16	0.14
1%Fe/CCBs ₄₀₀₋₁₀₀₀	400	1000	1.0	642	7.0	1.08	0.15
1%Mn/CCBs ₄₀₀₋₁₀₀₀	400	1000	1.0	643	8.0	1.06	0.15
0.5%Ni/CCBs ₄₀₀₋₆₀₀	400	600	0.5	750	8.0	1.55	0.18
1%Ni/CCBs ₄₀₀₋₆₀₀	400	600	1.0	763	8.0	1.59	0.18
5%Ni/CCBs ₄₀₀₋₆₀₀	400	600	5.0	708	8.0	1.41	0.15
1%Ni/CCBs ₂₀₀₋₁₀₀₀	200	1000	1.0	639	6.1	1.25	0.11
1%Ni/CCBs ₈₀₀₋₁₀₀₀	800	1000	1.0	553	22.2	2.14	0.16
1%Ni/CCBs ₄₀₀₋₁₄₀₀	400	1400	1.0	520	9.2	1.48	0.08
1%Ni/Q15 ^f	–	–	1.0	185	9.2	0.98	ND ^g
1%Ni/G-70R ^h	–	–	1.0	1230	ND	0.04	0.53

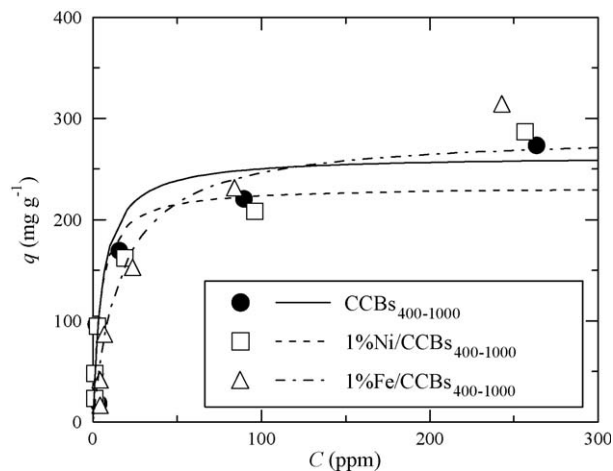
^a R_{load} : weight ratio of loaded metal oxide to support material.^b S_{BET} : BET specific surface area.^c R_{peak} : peak radius of mesopore size distribution.^d V_{mes} : mesopore volume.^e V_{mic} : micropore volume.^f Q15: commercial silica gel beads possessing almost the same pore diameter and mesopore volume as CCBs₄₀₀₋₁₀₀₀.^g ND: not detected.^h G-70R: commercial activated carbon beads with developed micropores.**Fig. 4.** (a) Adsorption and desorption isotherms of N₂ on CCBs₄₀₀₋₁₀₀₀ (circle) and 1%Ni/CCBs₄₀₀₋₁₀₀₀ (triangle), and (b) corresponding pore size distribution determined based on the Dollimore–Heal method.

phenol and its removal rate in a logarithmic scale. The removal rate constant and the order of removal process are determined by fitting the measured data to Equation (1) below.

$$\frac{-dC}{dt} = kC^n \quad (1)$$

where C , t , k and n respectively denote the concentration of phenol, treatment time, removal rate constant and the order of the removal process.

As shown in Table 3, the removal rate constant when using only CCBs₄₀₀₋₁₀₀₀ in the absence of ozone is 0.048 min⁻¹, whereas that when using ozone alone is estimated to be 0.073 min⁻¹. With simultaneous use of CCBs₄₀₀₋₁₀₀₀ with ozone, the constant can be increased to 0.151 min⁻¹. Interestingly, when using 1%Ni/CCBs₄₀₀₋₁₀₀₀ instead of CCBs₄₀₀₋₁₀₀₀, the rate constant increases to 0.207 min⁻¹, possibly due to the catalytic enhancement effect of the loaded nickel oxide. In the latter two cases, the removal rate includes the effects of both adsorption of phenol on CCBs and its degradation by ozone. Since the removal process of phenol when

**Fig. 5.** Liquid phase adsorption isotherms of phenol on CCBs and CCBs loaded with metal oxides (fitted curves: Langmuir model). Temperature = 30 °C.

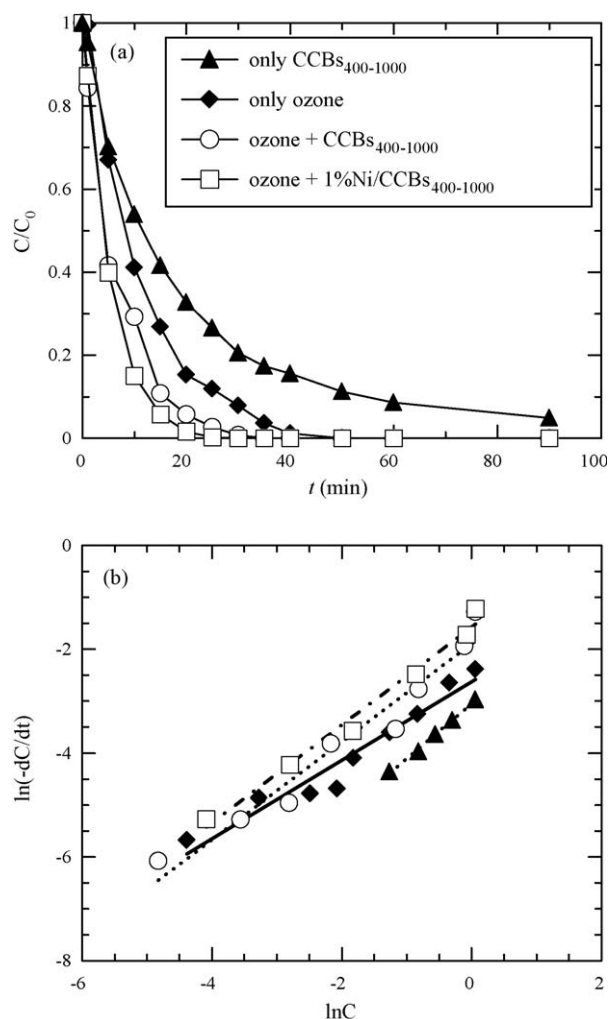


Fig. 6. (a) Changes with time in concentration of aqueous phenol during ozonation. (b) Relation between concentration of phenol and reaction rate. Temperature = 30 °C.

using CCBs₄₀₀₋₁₀₀₀ and 1%Ni/CCBs₄₀₀₋₁₀₀₀ can be approximately regarded as a 1st order process relative to the concentration of phenol as shown in Fig. 6(b), it is possible to conclude that the removal process can be enhanced by the adsorptive-concentration effect of CCBs as expected. Moreover, the advantage of loading metal oxides on CCBs can also be seen in Fig. 7, which shows the change with elapse of time in concentration of phenol during ozonation by the repetitive use of CCBs₄₀₀₋₁₀₀₀ or 1%Ni/CCBs₄₀₀₋₁₀₀₀. When CCBs₄₀₀₋₁₀₀₀ is used, the removal efficiency of phenol gradually decreases with increased iteration, due to the irreversible adsorption of phenol or reaction products formed by the degradation of phenol. On the other hand, when using 1%Ni/CCBs₄₀₀₋₁₀₀₀, the decrease in removal efficiency is significantly smaller than that when using CCBs₄₀₀₋₁₀₀₀. This result indicates

Table 3
Order of removal process, constant of removal rate and amount of leached metal.

	n	k (min ⁻¹)	R_{leach} (%)
Only CCBs ₄₀₀₋₁₀₀₀	1.056	0.048	–
Only ozone	0.756	0.073	–
Ozone + CCBs ₄₀₀₋₁₀₀₀	0.944	0.151	–
Ozone + 1%Ni/CCBs ₄₀₀₋₁₀₀₀	0.943	0.207	1.3
Ozone + 1%Co/CCBs ₄₀₀₋₁₀₀₀	0.880	0.155	16.0
Ozone + 1%Fe/CCBs ₄₀₀₋₁₀₀₀	0.836	0.158	0.9
Ozone + 1%Mn/CCBs ₄₀₀₋₁₀₀₀	0.993	0.200	50.7

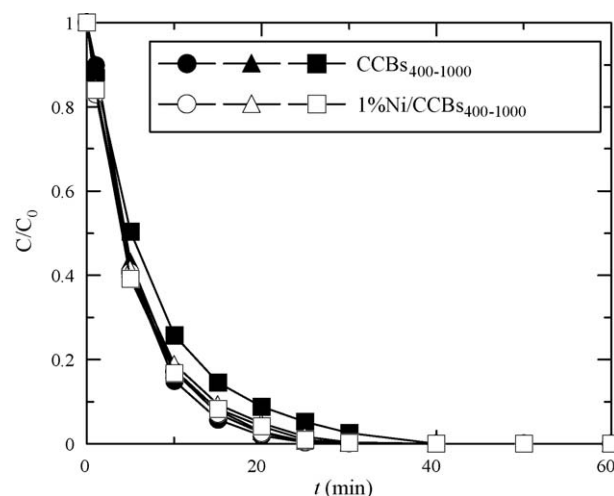


Fig. 7. Changes with time in concentration of aqueous phenol during ozonation using CCBs₄₀₀₋₁₀₀₀ without loading nickel oxide and 1%Ni/CCBs₄₀₀₋₁₀₀₀. circle: 1st measurement, triangle: 2nd measurement, square: 3rd measurement. Temperature = 30 °C.

that metal oxides loaded on CCBs can prevent irreversible adsorption of reaction products, which would otherwise cause a decrease in adsorption performance.

3.3. Effect of different conditions on removal efficiency of aqueous phenol

Changes with time in the concentration of aqueous phenol during ozonation using CCBs loaded with different metal oxides are shown in Fig. 8. As summarized in Table 3, of the metal species examined, nickel oxide and manganese oxide were confirmed to show the highest enhancement effect. However, the leached amount of manganese oxide during ozonation is greater than that of nickel oxide or iron oxide as shown in Table 3. Leaching of manganese oxide during ozonation leads to a decrease in catalytic performance. This is due to the acidic state of the treated water, as previously reported by Miró et al. [21]. Based on these results, nickel was determined as the most suitable catalyst for loading on CCBs.

Fig. 9 shows the effects of different support materials on the changes with time in the concentration of aqueous phenol during

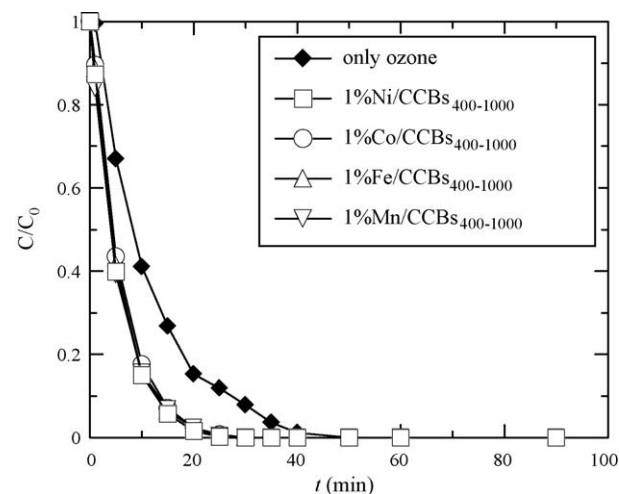


Fig. 8. Changes with time in concentration of aqueous phenol during ozonation using CCBs loaded with different metal species. Temperature = 30 °C.

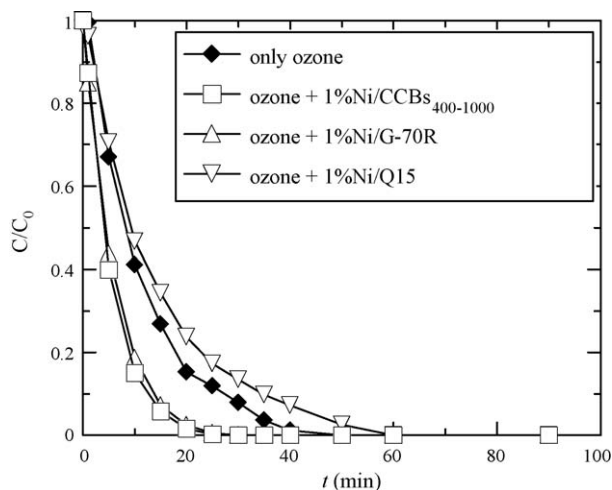


Fig. 9. Effect of different support materials on change with time in concentration of aqueous phenol during ozonation, G-70R: activated carbon beads with developed micropores, Q15: silica gel beads possessing almost the same pore diameter and mesopore volume as CCBs₄₀₀₋₁₀₀₀. Temperature = 30 °C.

ozonation. When using Q15, it is clear that adsorptive concentration of phenol does not occur, since the removal efficiency is lower than when using only ozone. This is due to the hydrophilic surface of the silica gels. On the other hand, the removal efficiency was significantly enhanced by using CCBs₄₀₀₋₁₀₀₀ and G-70R as support materials. It is noteworthy that the enhancement effect of CCBs₄₀₀₋₁₀₀₀ is greater than that of G-70R. This can be attributed to the difference in pore size between CCBs₄₀₀₋₁₀₀₀ and G-70R, since phenol or reaction products can diffuse more easily in mesopores than in micropores.

The effect on the removal efficiency of the amount of nickel oxide loaded on the CCBs was shown in Fig. 10. When using 1%Ni/CCBs₄₀₀₋₆₀₀, removal efficiency is greater than when using 0.5%Ni/CCBs₄₀₀₋₆₀₀, indicating that the degradation rate of phenol increases with increasing nickel oxide loaded. However, the removal efficiency when using 5%Ni/CCBs₄₀₀₋₆₀₀ is slightly lower than that when using 1%Ni/CCBs₄₀₀₋₆₀₀. Considering that the volume of mesopores in 5%Ni/CCBs₄₀₀₋₆₀₀ is slightly smaller than that in 1%Ni/CCBs₄₀₀₋₆₀₀, it is assumed that mesopores in 5%Ni/CCBs₄₀₀₋₆₀₀ are partially filled with the loaded nickel oxide, which limits the diffusion of phenol or reaction products and consequently leads to the decrease in removal efficiency.

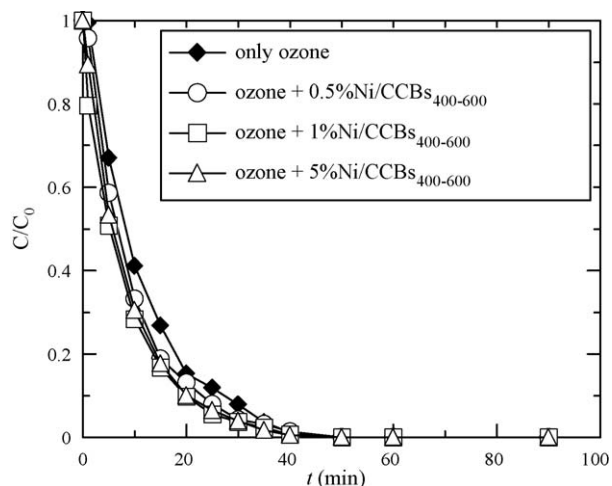


Fig. 10. Effect of loaded amount of nickel oxide on change with time in concentration of aqueous phenol during ozonation. Temperature = 30 °C.

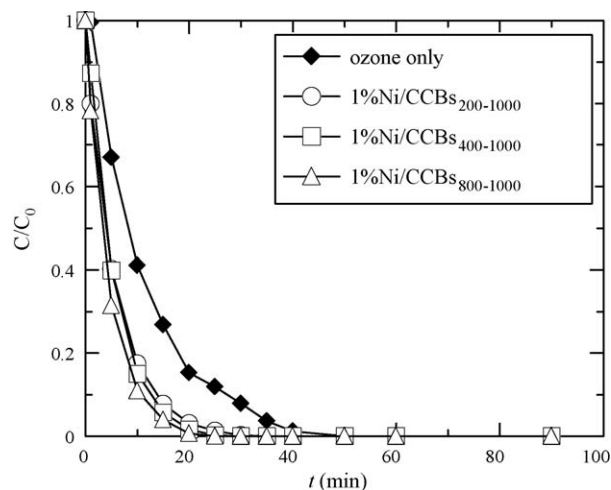


Fig. 11. Effect of size of mesopores in CCBs on change with time in concentration of aqueous phenol during ozonation. Temperature = 30 °C.

Fig. 11 shows the changes with time in concentration of phenol during ozonation using nickel oxide-loaded CCBs with a different mesopore size. It is noteworthy that the removal efficiency clearly increases with the increase in the size of mesopores. This is because the diffusion rate of phenol or reaction products increases increased size of mesopores in CCBs, as discussed above.

Fig. 12 shows the effect of carbonization temperature of CCBs on changes with elapse of time in phenol concentration during ozonation. It is noteworthy that the removal efficiency of phenol increases with increasing carbonization temperature. Since the size of mesopores increases with increased carbonization temperature as shown in Table 2, this tendency may be attributed to the difference in the size of mesopores as discussed above. However, this result cannot be explained simply by the porous properties of CCBs, considering that the volume of micropores, which are considered to act as adsorption sites of phenol, decreases with increasing carbonization temperature. Another possible reason is increased hydrophobicity, which can enhance the adsorptive-catalytic effect of CCBs, with increasing carbonization temperature. Since the increase in hydrophobicity is compensated by the decrease in adsorbed amount due to the decrease in micropores, the interaction between pores and phenol molecules

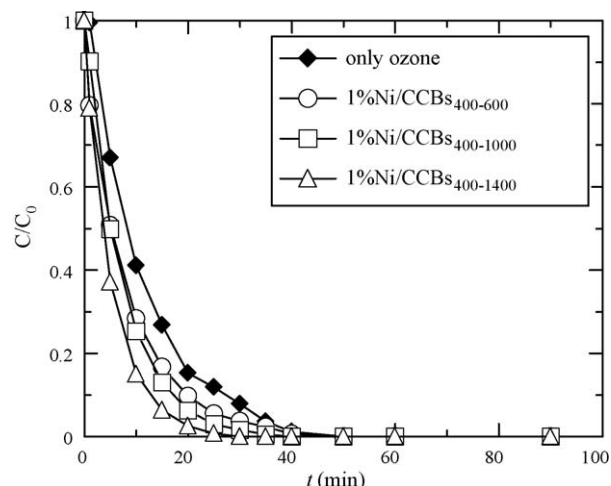


Fig. 12. Effect of carbonization temperature of CCBs on change with time in concentration of aqueous phenol during ozonation. Temperature = 30 °C.

can be enhanced. Further investigation is necessary to clarify the relationship between the adsorptive-concentration effect and surface properties of CCBs. These will be examined in a future study.

4. Conclusions

The potential for use of mesoporous carbon cryogel beads (CCBs) as adsorbents and support materials to remove aqueous organic pollutants was examined. Due to the adsorptive-concentration effect of the CCBs, the removal efficiency of aqueous phenol, used as a model pollutant, was significantly enhanced by the simultaneous use of ozone plus CCBs over ozone alone. Metal oxides loaded on CCBs further improved the removal of aqueous phenol. The parameters affecting the removal efficiency of the CCBs loaded with metal oxides included the size of the mesopores, the amount of loaded metal and the carbonization temperature during preparation of CCBs.

Although further studies will be needed to clarify the interaction between the hydrophobicity of the surface of CCBs and aqueous organic pollutants, we believe CCBs to be an advantageous adsorbent and support material of catalysts with potential for use in an advanced oxidation process for treating wastewater containing organic pollutants.

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